

## PATENT ABSTRACTS OF JAPAN

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(54) PAPER STRENGTH INTENSIFIER FOR NEUTRAL PAPERMAKING AND ITS APPLICATION

(57)Abstract:

PURPOSE: To obtain the subject intensifier exhibiting an excellent paper strength intensifying effect without reducing optical properties in a neutral papermaking condition by including (meth)acrylamide and a specific polymer.



CONSTITUTION: This paper strength intensifier in a neutral papermaking contains a copolymer comprising (A) (meth)acrylamide and (B) a vinyl compound expressed by formula I (R1 is H, a 1-3C alkyl) or its salt as constituting components. Furthermore, a paper strength intensifier in a neutral papermaking is obtained which contains a copolymer comprising 60-98.95mol% of the component A, 0.5-20mol% of the compound B, (C) 0.05-10mol% of a vinyl compound expressed by formula II (R2 is H or a 1-3C alkyl; (n) is 1-5) or its salt, and (D) 0.5-10mol% of an  $\alpha,\beta$ -unsaturated monocarboxylic acid or a polycarboxylic acid or a salt thereof as constituting components. The intensifiers exhibit a superior paper strength intensifying effect than usual intensifiers as for a specific bursting strength and a Z-direction tensile strength.



II

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CLAIMS

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[Claim(s)]

[Claim 1] (Meta) The neutral paper-making form force enhancement agent characterized by containing the copolymer which contains as a constituent the vinyl compounds expressed with acrylamide and the following general formula (1), or those salts.

$\text{CH}_2=\text{CR}_1-\text{COO}(\text{CH}_2)_3-\text{N}(\text{CH}_3)_2$  (1)

(The inside R1 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3.)

[Claim 2] (a) (meta) Acrylamide Compound of the 60-98.95-mol% and (b) aforementioned general formula (1) The 0.5-20-mol% and (c) following general formula (2)

$\text{CH}_2=\text{CR}_2-(\text{CH}_2)_n-\text{SO}_3\text{H}$  (2)

(The inside R2 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-5.) The vinyl compounds displayed or those salts 0.05-10-mol% and

(d) alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or those salts Neutral paper-making form force agent characterized by containing the copolymer which

contains 0.5-10-mol% as a constituent.

[Claim 3] A copolymer is a neutral paper-making form force agent according to claim 2 characterized by containing the vinyl compound in which copolymerization of further others is possible as a copolymer component.

[Claim 4] Paper using a neutral paper-making form force agent according to claim 1, 2, or 3.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a neutral paper-making form force enhancement agent.

[0002]

[Description of the Prior Art] On the paper-making conditions in the absence, a Pulse-Amplitude-Modulation (polyacrylamide) system paper reinforcing agent is widely used from current and acidity, and development of a high performance paper reinforcing agent is also progressing. However, the product with which a Pulse-Amplitude-Modulation system paper durability agent still fills a user's needs in neutral paper-making conditions (paper making pH is seven or more) is underdeveloped, and cationized starch is used widely.

[0003]

[Problem(s) to be Solved by the Invention] This invention offers the neutral paper-making form force enhancement agent which solves such a trouble.

[0004]

[Means for Solving the Problem] this invention persons came to accomplish invention of a paper reinforcing agent the fall of optical-character ability (a whiteness degree, blank paper opacity) excels [ invention ] in paper durability reinforcement few in neutral paper-making conditions, as a result of repeating examination wholeheartedly about the acrylamide (meta) system polymer which used the specific vinyl compound as the indispensable component. That is, this invention is the paper using the neutral paper-making form force enhancement agent characterized by containing the copolymer which contains as a constituent the vinyl compounds expressed with acrylamide (meta) and the following general formula (1), or those salts, and this paper reinforcing agent.

$\text{CH}_2=\text{CR}_1-\text{COO}(\text{CH}_2)_3-\text{N}(\text{CH}_3)_2$  (1)

(The inside R1 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3.)

[0005] The desirable mode of this invention is (a) (meta) acrylamide. Compound of the 60-98.95-mol% and (b) aforementioned general formula (1) The 0.5-20-mol% and (c) following general formula (2)

$\text{CH}_2=\text{CR}_2-(\text{CH}_2)_n-\text{SO}_3\text{H}$  (2)

(The inside R2 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-5.) The vinyl compounds displayed or those salts 0.05-10-mol% and (d) alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or those salts It is the neutral paper-making form force agent characterized by containing the copolymer which contains 0.5-10-mol% as a constituent. This invention is explained to a detail below.

[0006] The amount of the acrylamide (meta) in a copolymer is usually less than [ more than 60mol%98.95mol% ]. (Meta) Acrylamide is marketed in the state of fine particles or a water solution, and all can be used for it if usually used industrially. Moreover, even if it uses acrylamide and acrylamide (meta) together, they do not interfere.

[0007] In the vinyl compound of a general formula (1), R1 is a low-grade alkyl group, is the alkyl

group of carbon numbers 1-3 preferably, and is specifically a methyl group, an ethyl group, n-propyl group, and i-propyl group. The salt is a hydrochloride, a sulfate, etc. N and N-dimethylaminopropylacrylate, N, and N-dimethylaminopropyl methacrylate etc. can be illustrated as an example of a vinyl compound expressed with a general formula (1). these -- one sort -- or two or more sorts can be used. The amount of the vinyl compound expressed with a general formula (1) is usually less than [ more than 0.5mol%20mol% ], and is less than [ more than 3mol% 15mol% ] preferably. Less than [ 0.5mol% ], the effectiveness is not demonstrated, but if 20-mol% is exceeded, control of a polymerization reaction tends to become difficult.

[0008] In the vinyl compound expressed with said general formula (2), R2 is a low-grade alkyl group, is the alkyl group of carbon numbers 1-3 preferably, and is specifically a methyl group, an ethyl group, n-propyl group, and i-propyl group. The salt is alkali-metal salts, such as sodium and a potassium, ammonium salt, etc. As an example of a vinyl compound expressed with a general formula (2), an allyl compound sulfonic acid, sodium allylsulfonate, allyl compound sulfonic-acid ammonium, a metallyl sulfonic acid, sodium methallylsulfonate, metallyl sulfonic-acid ammonium, etc. can be illustrated, for example. these -- one sort -- or two or more sorts can be used. The amount of the vinyl compound expressed with a general formula (2) is usually less than [ more than 0.05mol%10mol% ], and is less than [ more than 0.1mol%7mol% ] preferably. Less than [ 0.05mol% ], the effectiveness is not demonstrated, but if ten-mol% is exceeded, control of a polymerization reaction tends to become difficult.

[0009] As an example of alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or its salt, an alkali-metal salt or ammonium salt, such as an acrylic acid, a methacrylic-acid crotonic acid, a sorbic acid, a citraconic acid, a maleic acid, an itaconic acid, fumaric acids or those sodium, and a potassium, etc. can be illustrated. these -- one sort -- or two or more sorts can be used. The amount of alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or its salt is usually less than [ more than 0.5mol%10mol% ], and is less than [ more than 1mol%7mol% ] preferably. Less than [ 0.5mol% ], the effectiveness is not demonstrated, but if ten-mol% is exceeded, the engine performance as a paper reinforcing agent will fall.

[0010] In addition, as a vinyl compound which can be copolymerized, a cationic vinyl compound, an anionic vinyl compound, etc. can be illustrated. As a cationic vinyl compound, the 3rd class amino system vinyl compound like dimethylaminoethyl (meta) acrylate and diethylaminoethyl (meta) acrylate, allylamine, a metallyl amine, etc. can illustrate those salts or the 4th class amino system vinyl compound further obtained in the amino group of these compounds by the reaction with the 4th class-ized agents, such as methyl chloride, a dimethyl sulfate, epichlorohydrin, or benzyl chloride, for example. Moreover, as an anionic vinyl compound, an alkali-metal salt or ammonium salt, such as 2-acrylamido-2-methyl propane sulfonic acid, a vinyl sulfonic acid, styrene sulfonic acids, those sodium salt, or potassium salt, etc. can be raised, for example.

[0011] As a vinyl compound besides these which can furthermore copolymerize other Methylene (screw) acrylamide, methylene (screw) meta-acrylamide, Diaryl acrylamide, triacrylformal, diacryloyl imide, Ethylene glycol diacrylate, ethylene glycol dimethacrylate, Propylene glycol diacrylate, 1, 3-butylene-glycol dimethacrylate, 1, 4-butylene-glycol dimethacrylate, trimethylolpropane triacrylate, The vinyl compound of cross-linking, such as a divinylbenzene and diallyl phthalate, Acrylonitrile, dimethyl acrylamide, a methyl methacrylate, (Meta) Allyl alcohol, methallyl alcohol, allyl compound methacrylate, an allyl chloride, Methallyl chloride, an allyl compound cyanide, a metallyl cyanide, allyl compound benzene, Metallyl benzene, allylacetone, a metallyl acetone, glycidyl methacrylate, Methacrylic-acid benzyl, hydroxymethyl methacrylate, hydroxyethyl acrylate, styrene, alpha methyl styrene, an alpha-methyl-styrene dimer, etc. can be illustrated.

[0012] These can use suitably one sort or two sorts or more of compounds according to the purpose. Less than [ 30 mol % ] is desirable still more desirable, and the addition of the vinyl compound which can copolymerize other is less than [ 15 mol % ]. When 30-mol % is exceeded, the fall of the effectiveness as a paper reinforcing agent is seen.

[0013] The method of manufacturing the copolymer of this invention can use a well-known polymerization method, for example, aqueous polymerization, a precipitation polymerization, an

emulsion polymerization, etc. Moreover, which combination of a batch polymerization and a half-batch polymerization is sufficient, and a polymerization method is not restricted at all. For example, addition mixing is carried out at an above-mentioned rate which sets the vinyl compound which can be copolymerized in addition to this as the purpose acrylamide (meta), a general formula (1), the vinyl compound further expressed with a general formula (2) or its salt, alpha, beta partial saturation monocarboxylic acid, polycarboxylic acid or its salt, and if needed, and it adjusts to desired pH, warms at 10-95 degrees C under aqueous intermediation, and can manufacture by adding and carrying out the polymerization of the polymerization initiator for 1-10 hours.

[0014] Polymerization temperature changes with the class of polymerization initiator, and amounts. Moreover, although it is influenced by those physical properties when adding the vinyl compound which can copolymerize other, 10-95 degrees C is usually 20-90 degrees C preferably. Moreover, the concentration of the vinyl compound at the time of a polymerization is 5 - 50 % of the weight, and is 10 - 40 % of the weight preferably.

[0015] As a polymerization initiator, the superphosphate like the bromate like a hydrogen peroxide, the peroxide like a benzoyl peroxide, sodium persulfate, potassium persulfate, the persulfate like ammonium persulfate, sodium bromate, and a potassium bromate, sodium perborate, a perboric acid potassium, the perboric acid salt like perboric acid ammonium, a fault sodium carbonate, potassium percarbonate, the percarbonate like a fault ammonium carbonate, perphosphoric acid sodium, a perphosphoric acid potassium, and perphosphoric acid ammonium etc. is mentioned, for example. Furthermore, 2 and 2'-azobis (2-amidinopropane) dihydrochloride, 2 and 2'-azobis [2-(5-methyl-2-imidazoline-2-IRU) propane] dihydrochloride, 2 and 2'-azobis [2-(2-imidazoline-2-IRU) propane] dihydrochloride, 2 and 2'-azobis [2-(2-imidazoline-2-IRU) propane], 2 and 2' - azobis [a 2-methyl-N-[1 and 1'-screw (hydroxymethyl)-2-hydroxyethyl] propione amide] -- - azobis (2-methyl propione amide) JIHIDO rate, and 2 and 2'-azobis [2-methyl-N-(2-hydroxyethyl) propione amide], 2, and 2' 4, 4'-azobis (4-cyano valeric acid) etc. can be used. Moreover, it is also possible to perform the polymerization method which makes a reducing agent live together in the aforementioned oxidizer, i.e., redox polymerization. As a reducing agent used for redox polymerization, water-soluble inorganic reducing agents, such as the iron like a ferrous sulfate and ferrous chloride, sodium bisulfite, potassium bisulfite, the sodium metabisulfite, potassium metabisulfite, a sodium thiosulfate, potassium thiosulfate, a sodium nitrite, and a sodium sulfite, are mentioned. The addition of a polymerization initiator is usually used in 0.001 - 5% of the weight of the range to all vinyl compounds. As a pH regulator, alkalization agents, such as a sodium hydroxide, a potassium hydroxide, and ammonia, and a phosphoric acid, a sulfuric acid, a hydrochloric acid, etc. are mentioned, for example.

[0016] The paper reinforcing agent of this invention is usually used by the following approaches. That is, in a pulp slurry, paper-making pH adjustment is performed by the sulfuric acid or the sodium hydroxide, the aluminum sulfate of the specified quantity is added if needed, stirring, and then this paper reinforcing agent is added. Although especially the addition sequence of an aluminum sulfate and this paper reinforcing agent is not asked, when it attaches importance to especially the water break on a wire at the time of paper making, the approach of adding an aluminum sulfate previously and then adding this paper reinforcing agent is desirable. After paper making, press dehydration is performed, it dries with a drum dryer, and \*\*\*\* is obtained. 0.05 - 3.0 % of the weight is usually suitable for the paper reinforcing agent contained in this \*\*\*\* as solid content. The paper reinforcing agent obtained by the approach of this invention is a paper reinforcing agent which has a large effective paper-making pH field, and has high paper durability reinforcement.

[0017]

[Example] Hereafter, although an example explains this invention to a detail, this invention is not limited to these examples.

[0018] The temperature up of the temperature is carried out to 50 degrees C, adding acrylamide 500g, dimethylaminopropyl methacrylate 33.08g, and 243.8g of city waters to the 1l. 4-inlet separable flask equipped with example 1 stirrer, a thermometer, a reflux condenser, and nitrogen installation tubing 40%, adjusting pH to 4.2, and performing a nitrogen purge. After adding and

carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7300cps in 25 degrees C and pH4.6 was obtained. This product is set to A.

[0019] The temperature up of the temperature is carried out to 50 degrees C, adding 40% acrylamide 319g, meta-acrylamide 9.05g, 1.55g [ of sodium methallylsulfonate ], and dimethylaminopropyl methacrylate 25.49g, 2.87g [ of 80% acrylic acids ], 4.15g [ of itaconic acids ], and methylenebis acrylamide 0.33g, and 773.2g of city waters to the same separable flask as example 2 example 1, adjusting pH to 4.2, and performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 4000cps in 25 degrees C and pH4.4 was obtained. This product is set to B.

[0020] 40% acrylamide 319g, 3.08g [ of sodium methallylsulfonate ], and dimethylaminopropyl methacrylate 23.93g, methylene (screw) acrylamide 0.31g, 7.8g of itaconic acids, and 729.85g of city waters are added to the same separable flask as example 3 example 1, pH is adjusted 4.2 times, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7000cps in 25 degrees C and pH4.7 was obtained. This product is set to C.

[0021] 40% acrylamide 319g, dimethylaminopropyl methacrylate 23.93g, 2.7g [ of 80% acrylic acids ], 3.1g [ of sodium methallylsulfonate ], and methylene (screw) acrylamide 0.31g, 3.9g of itaconic acids, and 719.5g of city waters are added to the same separable flask as example 4 example 1, pH is adjusted 4.2 times, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6300cps in 25 degrees C and pH4.4 was obtained. This product is set to D.

[0022] The temperature up of the temperature is carried out to 50 degrees C, adding acrylamide 500g, dimethylaminoethyl methacrylate 32.65g, and 242.8g of city waters to the same separable flask as example of comparison 1 example 1 40%, adjusting pH to 4.2, and performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6700cps in 25 degrees C and pH4.3 was obtained. This product is set to E. The presentation of the polymer of the above examples 1-4 and the example 1 of a comparison was collectively shown in Table 1.

[0023]

[Table 1]

表 1  
組成表 (モル%表示)

	Am	MAm	DM	DMP	AA	ITA	MBA	SMS
実施例 1	93	-	-	7	-	-	-	-
実施例 2	84.4	5	-	7	1.5	1.5	0.1	0.5
実施例 3	89.9	-	-	7	-	3	0.1	1.0
実施例 4	89.9	-	-	7	1.5	1.5	0.1	1.0
比較例 1	93	-	7	-	-	-	-	-

Am Acrylamide MAm Meta-acrylamide SMS Sodium methallylsulfonate DM N. and N-dimethylaminoethyl methacrylate DMP N and N-dimethylaminopropyl methacrylate AA Acrylic-acid MBA Methylenebis acrylamide ITA Itaconic acid [0024] the pulp slur of 1.0% of concentration which is the freshness (it is described as Canadian standard freshness and following c.s.f) of 500ml obtained from applications 1-4 and comparison application 1LBKP -- an aluminum sulfate -- dry weight criteria -- 0.3% for pulp -- it added and stirred for 1 minute. The sodium hydroxide was beforehand added and adjusted so that pH of a pulp slurry might be set to 7.5 at this time. subsequently, the paper reinforcing agent obtained in the example 1 -- desiccation criteria -- 0.3% for pulp -- measurement of freshness (JIS-P8121) and paper making with a TAPPI square shape sheet machine were performed using the pulp slurry which added, continues stirring for 1 more minute and might be added under stirring of a sizing compound, a calcium carbonate, and a yield improver after that. The wet sheet which carried out paper making performs 110 degrees C and desiccation during 1 minute with the rear-drum dryer of a press, and is basis-weight 100 g/m<sup>2</sup>. The handmade paper was obtained. Let this \*\*\*\* be an application 1. JIS after performing seasoning of 24 hours or more for obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room -- law -- following -- a ratio -- measurement of bursting strength (JIS-P8112), Z-axis reinforcement (it measures by the internal bond tester by Kumagaya Riki Kogyo K.K.), and blank paper opacity (JIS-P8183) was performed. In the approach of obtaining the converted paper of an application 1, the paper of applications 2-4 and the comparison application 1 was completely obtained in the same conditions and identity operation except changing the paper reinforcing agent (A) of an example 1. moreover, the ratio of the paper of applications 2-4 and the comparison application 1 -- measurement of bursting strength, freshness, Z-axis reinforcement, and blank paper opacity was also completely performed in the same conditions and identity operation with evaluation of the paper of an application 1. Those results were shown in Table 2.

[0025]

[Table 2]



表2 (紙力増強剤添加量0.3%)

	添加樹脂	比破裂強度 Kgf/cm <sup>2</sup>	濾水度 ml	Z軸強度	白紙不透明度
	無添加	2.56	440	3.20	85.3
応用例1	A	3.19	560	4.90	86.4
応用例2	B	3.31	480	4.83	87.3
応用例3	C	3.20	510	4.70	86.8
応用例4	D	3.29	475	4.80	87.0
比較応用例1	E	3.00	500	4.41	86.3

[0026]

[Effect of the Invention] without, as for the paper reinforcing agent by this invention, optical-character ability falls in neutral paper-making conditions as compared with the conventional paper reinforcing agent -- a ratio -- it is in \*\* from Table 2nd that it is the outstanding paper reinforcing agent which shows the paper durability effectiveness which was excellent in bursting strength and Z-axis reinforcement.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to a neutral paper-making form force enhancement agent.

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PRIOR ART

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[Description of the Prior Art] On the paper-making conditions in the acescence, a Pulse-Amplitude-Modulation (polyacrylamide) system paper reinforcing agent is widely used from current and acidity, and development of a high performance paper reinforcing agent is also progressing. However, the product with which a Pulse-Amplitude-Modulation system paper durability agent still fills a user's needs in neutral paper-making conditions (paper making pH is seven or more) is underdeveloped, and cation-ized starch is used widely.

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EFFECT OF THE INVENTION

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[Effect of the Invention] without, as for the paper reinforcing agent by this invention, optical-character ability falls in neutral paper-making conditions as compared with the conventional paper reinforcing agent -- a ratio -- it is in \*\* from Table 2nd that it is the outstanding paper reinforcing agent which shows the paper durability effectiveness which was excellent in bursting strength and Z-axis reinforcement.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention offers the neutral paper-making form force enhancement agent which solves such a trouble.

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MEANS

[Means for Solving the Problem] this invention persons came to accomplish invention of a paper reinforcing agent the fall of optical-character ability (a whiteness degree, blank paper opacity) excels [ invention ] in paper durability reinforcement few in neutral paper-making conditions, as a result of repeating examination wholeheartedly about the acrylamide (meta) system polymer which used the specific vinyl compound as the indispensable component. That is, this invention is the paper using the neutral paper-making form force enhancement agent characterized by containing the copolymer which contains as a constituent the vinyl compounds expressed with acrylamide (meta) and the following general formula (1), or those salts, and this paper reinforcing agent.



(The inside R1 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3.)

[0005] The desirable mode of this invention is (a) (meta) acrylamide. Compound of the 60-98.95-mol% and (b) aforementioned general formula (1) The 0.5-20-mol% and (c) following general formula (2)



(The inside R2 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-5.) The vinyl compounds displayed or those salts 0.05-10-mol% and (d) alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or those salts It is the neutral paper-making form force agent characterized by containing the copolymer which contains 0.5-10-mol% as a constituent. This invention is explained to a detail below.

[0006] The amount of the acrylamide (meta) in a copolymer is usually less than [ more than 60mol%98.95mol% ]. (Meta) Acrylamide is marketed in the state of fine particles or a water solution, and all can be used for it if usually used industrially. Moreover, even if it uses acrylamide and acrylamide (meta) together, they do not interfere.

[0007] In the vinyl compound of a general formula (1), R1 is a low-grade alkyl group, is the alkyl group of carbon numbers 1-3 preferably, and is specifically a methyl group, an ethyl group, n-propyl group, and i-propyl group. The salt is a hydrochloride, a sulfate, etc. N and N-dimethylaminopropylacrylate, N, and N-dimethylaminopropyl methacrylate etc. can be illustrated as an example of a vinyl compound expressed with a general formula (1). these -- one sort -- or two or more sorts can be used. The amount of the vinyl compound expressed with a general formula (1) is usually less than [ more than 0.5mol%20mol% ], and is less than [ more than 3mol% 15mol% ] preferably. Less than [ 0.5mol% ], the effectiveness is not demonstrated, but if 20-mol% is exceeded, control of a polymerization reaction tends to become difficult.

[0008] In the vinyl compound expressed with said general formula (2), R2 is a low-grade alkyl group, is the alkyl group of carbon numbers 1-3 preferably, and is specifically a methyl group, an ethyl group, n-propyl group, and i-propyl group. The salt is alkali-metal salts, such as sodium and a potassium, ammonium salt, etc. As an example of a vinyl compound expressed with a general formula (2), an allyl compound sulfonic acid, sodium allylsulfonate, allyl compound sulfonic-acid ammonium, a metallyl sulfonic acid, sodium methallylsulfonate, metallyl sulfonic-acid ammonium, etc. can be illustrated, for example. these -- one sort -- or two or more sorts can be used. The

amount of the vinyl compound expressed with a general formula (2) is usually less than [ more than 0.05mol%10mol% ], and is less than [ more than 0.1mol%7mol% ] preferably. Less than [ 0.05mol% ], the effectiveness is not demonstrated, but if ten-mol% is exceeded, control of a polymerization reaction tends to become difficult.

[0009] As an example of alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or its salt, an alkali-metal salt or ammonium salt, such as an acrylic acid, a methacrylic-acid crotonic acid, a sorbic acid, a citraconic acid, a maleic acid, an itaconic acid, fumaric acids or those sodium, and a potassium, etc. can be illustrated. these -- one sort -- or two or more sorts can be used. The amount of alpha and beta-partial saturation monocarboxylic acid, polycarboxylic acid, or its salt is usually less than [ more than 0.5mol%10mol% ], and is less than [ more than 1mol%7mol% ] preferably. Less than [ 0.5mol% ], the effectiveness is not demonstrated, but if ten-mol% is exceeded, the engine performance as a paper reinforcing agent will fall.

[0010] In addition, as a vinyl compound which can be copolymerized, a cationic vinyl compound, an anionic vinyl compound, etc. can be illustrated. As a cationic vinyl compound, the 3rd class amino system vinyl compound like dimethylaminoethyl (meta) acrylate and diethylaminoethyl (meta) acrylate, allylamine, a metallyl amine, etc. can illustrate those salts or the 4th class amino system vinyl compound further obtained in the amino group of these compounds by the reaction with the 4th class-ized agents, such as methyl chloride, a dimethyl sulfate, epichlorohydrin, or benzyl chloride, for example. Moreover, as an anionic vinyl compound, an alkali-metal salt or ammonium salt, such as 2-acrylamido-2-methyl propane sulfonic acid, a vinyl sulfonic acid, styrene sulfonic acids, those sodium salt, or potassium salt, etc. can be raised, for example.

[0011] As a vinyl compound besides these which can furthermore copolymerize other Methylene (screw) acrylamide, methylene (screw) meta-acrylamide, Diaryl acrylamide, triacrylformal, diacryloyl imide, Ethylene glycol diacrylate, ethylene glycol dimethacrylate, Propylene glycol diacrylate, 1, 3-butylene-glycol dimethacrylate, 1, 4-butylene-glycol dimethacrylate, trimethylolpropane triacrylate, The vinyl compound of cross-linking, such as a divinylbenzene and diallyl phthalate, Acrylonitrile, dimethyl acrylamide, a methyl methacrylate, (Meta) Allyl alcohol, methallyl alcohol, allyl compound methacrylate, an allyl chloride, Methallyl chloride, an allyl compound cyanide, a metallyl cyanide, allyl compound benzene, Metallyl benzene, allylacetone, a metallyl acetone, glycidyl methacrylate, Methacrylic-acid benzyl, hydroxymethyl methacrylate, hydroxyethyl acrylate, styrene, alpha methyl styrene, an alpha-methyl-styrene dimer, etc. can be illustrated.

[0012] These can use suitably one sort or two sorts or more of compounds according to the purpose. Less than [ 30 mol % ] is desirable still more desirable, and the addition of the vinyl compound which can copolymerize other is less than [ 15 mol % ]. When 30-mol % is exceeded, the fall of the effectiveness as a paper reinforcing agent is seen.

[0013] The method of manufacturing the copolymer of this invention can use a well-known polymerization method, for example, aqueous polymerization, a precipitation polymerization, an emulsion polymerization, etc. Moreover, which combination of a batch polymerization and a half-batch polymerization is sufficient, and a polymerization method is not restricted at all. For example, addition mixing is carried out at an above-mentioned rate which sets the vinyl compound which can be copolymerized in addition to this as the purpose acrylamide (meta), a general formula (1), the vinyl compound further expressed with a general formula (2) or its salt, alpha, beta partial saturation monocarboxylic acid, polycarboxylic acid or its salt, and if needed, and it adjusts to desired pH, warms at 10-95 degrees C under aqueous intermediation, and can manufacture by adding and carrying out the polymerization of the polymerization initiator for 1-10 hours.

[0014] Polymerization temperature changes with the class of polymerization initiator, and amounts. Moreover, although it is influenced by those physical properties when adding the vinyl compound which can copolymerize other, 10-95 degrees C is usually 20-90 degrees C preferably. Moreover, the concentration of the vinyl compound at the time of a polymerization is 5 - 50 % of the weight, and is 10 - 40 % of the weight preferably.

[0015] As a polymerization initiator, the superphosphate like the bromate like a hydrogen

peroxide, the peroxide like a benzoyl peroxide, sodium persulfate, potassium persulfate, the persulfate like ammonium persulfate, sodium bromate, and a potassium bromate, sodium perborate, a perboric acid potassium, the perboric acid salt like perboric acid ammonium, a fault sodium carbonate, potassium percarbonate, the percarbonate like a fault ammonium carbonate, perphosphoric acid sodium, a perphosphoric acid potassium, and perphosphoric acid ammonium etc. is mentioned, for example. Furthermore, 2 and 2'-azobis (2-amidinopropane) dihydrochloride, 2 and 2'-azobis [2-(5-methyl-2-imidazoline-2-IRU) propane] dihydrochloride, 2 and 2'-azobis [2-(2-imidazoline-2-IRU) propane] dihydrochloride, 2 and 2'-azobis [2-(2-imidazoline-2-IRU) propane], 2 and 2' - azobis [a 2-methyl-N-[1 and 1'-screw (hydroxymethyl)-2-hydroxyethyl] propione amide] -- - azobis (2-methyl propione amide) JIHIDO rate, and 2 and 2'-azobis [2-methyl-N-(2-hydroxyethyl) propione amide], 2, and 2 '4, 4'-azobis (4-cyano valeric acid) etc. can be used. Moreover, it is also possible to perform the polymerization method which makes a reducing agent live together in the aforementioned oxidizer, i.e., redox polymerization. As a reducing agent used for redox polymerization, water-soluble inorganic reducing agents, such as the iron like a ferrous sulfate and ferrous chloride, sodium bisulfite, potassium bisulfite, the sodium metabisulfite, potassium metabisulfite, a sodium thiosulfate, potassium thiosulfate, a sodium nitrite, and a sodium sulfite, are mentioned. The addition of a polymerization initiator is usually used in 0.001 - 5% of the weight of the range to all vinyl compounds. As a pH regulator, alkalization agents, such as a sodium hydroxide, a potassium hydroxide, and ammonia, and a phosphoric acid, a sulfuric acid, a hydrochloric acid, etc. are mentioned, for example.

[0016] The paper reinforcing agent of this invention is usually used by the following approaches. That is, in a pulp slurry, paper-making pH adjustment is performed by the sulfuric acid or the sodium hydroxide, the aluminum sulfate of the specified quantity is added if needed, stirring, and then this paper reinforcing agent is added. Although especially the addition sequence of an aluminum sulfate and this paper reinforcing agent is not asked, when it attaches importance to especially the water break on a wire at the time of paper making, the approach of adding an aluminum sulfate previously and then adding this paper reinforcing agent is desirable. After paper making, press dehydration is performed, it dries with a drum dryer, and \*\*\*\* is obtained. 0.05 - 3.0 % of the weight is usually suitable for the paper reinforcing agent contained in this \*\*\*\* as solid content. The paper reinforcing agent obtained by the approach of this invention is a paper reinforcing agent which has a large effective paper-making pH field, and has high paper durability reinforcement.

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[Translation done.]



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EXAMPLE

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[Example] Hereafter, although an example explains this invention to a detail, this invention is not limited to these examples.

[0018] The temperature up of the temperature is carried out to 50 degrees C, adding acrylamide 500g, dimethylaminopropyl methacrylate 33.08g, and 243.8g of city waters to the 1l. 4-inlet separable flask equipped with example 1 stirrer, a thermometer, a reflux condenser, and nitrogen installation tubing 40%, adjusting pH to 4.2, and performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7300cps in 25 degrees C and pH4.6 was obtained. This product is set to A.

[0019] The temperature up of the temperature is carried out to 50 degrees C, adding 40% acrylamide 319g, meta-acrylamide 9.05g, 1.55g [ of sodium methallylsulfonate ], and dimethylaminopropyl methacrylate 25.49g, 2.87g [ of 80% acrylic acids ], 4.15g [ of itaconic acids ], and methylenebis acrylamide 0.33g, and 773.2g of city waters to the same separable flask as example 2 example 1, adjusting pH to 4.2, and performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 4000cps in 25 degrees C and pH4.4 was obtained. This product is set to B.

[0020] 40% acrylamide 319g, 3.08g [ of sodium methallylsulfonate ], and dimethylaminopropyl methacrylate 23.93g, methylene (screw) acrylamide 0.31g, 7.8g of itaconic acids, and 729.85g of city waters are added to the same separable flask as example 3 example 1, pH is adjusted 4.2 times, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7000cps in 25 degrees C and pH4.7 was obtained. This product is set to C.

[0021] 40% acrylamide 319g, dimethylaminopropyl methacrylate 23.93g, 2.7g [ of 80% acrylic acids ], 3.1g [ of sodium methallylsulfonate ], and methylene (screw) acrylamide 0.31g, 3.9g of itaconic acids, and 719.5g of city waters are added to the same separable flask as example 4 example 1, pH is adjusted 4.2 times, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6300cps in 25 degrees C and pH4.4 was obtained. This product is set to D.

[0022] The temperature up of the temperature is carried out to 50 degrees C, adding acrylamide 500g, dimethylaminoethyl methacrylate 32.65g, and 242.8g of city waters to the same separable flask as example of comparison 1 example 1 40%, adjusting pH to 4.2, and performing a nitrogen purge. After adding and carrying out the polymerization of the potassium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6700cps in 25 degrees C and pH4.3

was obtained. This product is set to E. The presentation of the polymer of the above examples 1-4 and the example 1 of a comparison was collectively shown in Table 1.

[0023]

[Table 1]

表 1

組成表 (モル%表示)

	Am	MAm	DM	DMP	AA	ITA	MBA	SMS
実施例 1	93	-	-	7	-	-	-	-
実施例 2	84.4	5	-	7	1.5	1.5	0.1	0.5
実施例 3	89.9	-	-	7	-	3	0.1	1.0
実施例 4	89.9	-	-	7	1.5	1.5	0.1	1.0
比較例 1	93	-	7	-	-	-	-	-

Am Acrylamide MAm Meta-acrylamide SMS Sodium methallylsulfonate DM N and N-dimethylaminoethyl methacrylate DMP N and N-dimethylaminopropyl methacrylate AA Acrylic-acid MBA Methylenebis acrylamide ITA Itaconic acid [0024] the pulp slur of 1.0% of concentration which is the freshness (it is described as Canadian standard freshness and following c.s.f) of 500ml obtained from applications 1-4 and comparison application 1LBKP -- an aluminum sulfate -- dry weight criteria -- 0.3% for pulp -- it added and stirred for 1 minute. The sodium hydroxide was beforehand added and adjusted so that pH of a pulp slurry might be set to 7.5 at this time. subsequently, the paper reinforcing agent obtained in the example 1 -- desiccation criteria -- 0.3% for pulp -- measurement of freshness (JIS-P8121) and paper making with a TAPPI square shape sheet machine were performed using the pulp slurry which added, continues stirring for 1 more minute and might be added under stirring of a sizing compound, a calcium carbonate, and a yield improver after that. The wet sheet which carried out paper making performs 110 degrees C and desiccation during 1 minute with the rear-drum dryer of a press, and is basis-weight 100 g/m<sup>2</sup>. The handmade paper was obtained. Let this \*\*\*\* be an application 1. JIS after performing seasoning of 24 hours or more for obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room -- law -- following -- a ratio -- measurement of bursting strength (JIS-P8112), Z-axis reinforcement (it measures by the internal bond tester by Kumagaya Riki Kogyo K.K.), and blank paper opacity (JIS-P8183) was performed. In the approach of obtaining the converted paper of an application 1, the paper of applications 2-4 and the comparison application 1 was completely obtained in the same conditions and identity operation except changing the paper reinforcing agent (A) of an example 1. moreover, the ratio of the paper of applications 2-4 and the comparison application 1 -- measurement of bursting strength, freshness, Z-axis reinforcement, and blank paper opacity was also completely performed in the same conditions and identity operation with evaluation of the paper of an application 1. Those results were shown in Table 2.

[0025]

[Table 2]

表2 (紙力増強剤添加量0.3%)

	添加樹脂	比破裂強度 Kgf/cm <sup>2</sup>	濾水度 ml	Z軸強度	白紙不透明度
	無添加	2.56	440	3.20	85.3
応用例1	A	3.19	560	4.90	86.4
応用例2	B	3.31	480	4.83	87.3
応用例3	C	3.20	510	4.70	86.8
応用例4	D	3.29	475	4.80	87.0
比較応用例1	E	3.00	500	4.41	86.3

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[Translation done.]